

## COAL DEMINERALIZATION WITH HOT ALKALINE SOLUTIONS

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### INTRODUCTION

A process for extracting most of the mineral matter from coal was demonstrated recently (1). It involves treating fine-size coal with a hot alkaline solution to dissolve quartz and to convert clay minerals and iron pyrite into acid-soluble compounds which are extracted with dilute acid in a second step. Although various alkalis and acids may be utilized,  $\text{Na}_2\text{CO}_3$  and  $\text{H}_2\text{SO}_4$  are advantageous because of low cost and ready availability. Preliminary work has shown that hot  $\text{Na}_2\text{CO}_3$  solutions readily convert kaolinite into sodium hydroaluminosilicates which are acid-soluble (2). That work has also shown that hot sodium carbonate solutions will dissolve quartz and convert iron pyrite into hematite, but not as readily as sodium hydroxide solutions.

In this work, the characteristics of the two-step process were studied in greater detail using three different bituminous coals under a variety of conditions, with particular attention being given to the first step. The relative effectiveness of various alkalis was studied as well as the effects of alkali concentration, alkaline treatment time, and temperature. The alkali-treated coals were subsequently leached with hot  $\text{HNO}_3$  to remove mineral matter. Nitric acid was employed because it dissolves iron pyrite and is used for that purpose in ASTM Method D2492 (3) for determining various forms of sulfur in coal. Since only organically bound sulfur should remain in coal which has been leached with  $\text{HNO}_3$ , it was possible to obtain an indication of how much organic sulfur was removed by the two-step treatment.

### EXPERIMENTAL METHODS

Bituminous coals were obtained from several sources for this study (Table 1). Much of the work was done with high volatile C bituminous coal from the Lovilia No. 4 underground mine in Iowa. The other two coals were somewhat higher in rank. The different coals were ground to -200 mesh (U.S. Standard); a portion of each product was ball-milled further to approximately 90% -400 mesh. A sample of each prepared coal was leached with boiling dilute  $\text{HNO}_3$  to remove inorganic sulfur so that the sulfur content of the residue would reflect the organic sulfur content of the raw coal. The leaching procedure was similar to that of ASTM Method D2492 (3) and was described in more detail elsewhere (4).

For the first step, 12 g. of ground coal and 120 ml. of alkaline solution were mixed and placed in a 300-ml. stainless steel autoclave equipped with a turbine agitator. The system was flushed with nitrogen and then heated to the desired temperature while the mixture was stirred continuously. After a period of treatment at constant temperature and pressure, the autoclave was cooled quickly, and the contents were filtered to recover the coal. The filter cake was washed with 400 ml. of distilled water, dried at 90°C for 4 hr., weighed, and analyzed for total sulfur and ash. A portion of the alkali-treated coal (usually 2.5-3.0 g) was leached for an additional 30 min. with boiling 2.1 M  $\text{HNO}_3$  in a stirred, three-neck Pyrex flask fitted with a reflux condenser. In most cases, 250-300 ml. of acid was employed. After the acid treatment, the flask was cooled quickly to room temperature, and the

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contents were filtered. The filter cake was washed, dried, weighed, and analyzed as above. The ash content of the raw and treated coals was determined by ASTM Method D3174 (3), while the sulfur content was determined with a Fisher model 475 total sulfur analyzer.

#### REPORTING BASIS

The ash content of raw and treated coals is reported on a moisture-free basis and the sulfur content on both a moisture- and ash-free basis. The ash reduction achieved corresponds to the overall change in moisture-free ash content divided by the moisture-free ash content of the raw coal. The reduction in total sulfur content corresponds to the change in total sulfur content divided by the total sulfur content of the raw coal, all on a moisture- and ash-free basis. The apparent reduction in organic sulfur content corresponds to the difference between the sulfur content of the acid-leached raw coal and the final sulfur content of the acid-leached, alkali-treated coal divided by the sulfur content of the acid-leached raw coal, all on a moisture- and ash-free basis. Coal recovery corresponds to the mass ratio of coal recovered during the alkaline treatment step to coal charged, all on a moisture- and ash-free basis.

#### EXPERIMENTAL RESULTS

The results of leaching ground raw coals with  $\text{HNO}_3$  alone are indicated in Table 1. The sulfur content of the acid-leached coal is indicative of the organically bound sulfur, while the ash content reflects the removal of iron pyrite and other minerals such as carbonates which are soluble in nitric acid. It can be seen that acid leaching alone reduced the sulfur content of Cherokee coal by 57%, Illinois No. 6 coal by 44-55%, and Lower Kittanning coal by 84-87%; also for these coals the ash content was reduced by 63%, 44-56%, and 55-57%, respectively.

For the alkaline treatment experiments, a relatively long time was needed to heat the reactor and its contents to the required temperature. Typically, it took 20 min. to reach 150°C, 25 min. to reach 200°C, and 45 min. to reach 300°C. While the temperature was being raised, the alkaline attack on the coal and its mineral matter got underway. This attack can be seen from the changes which took place when ball-milled Cherokee coal was heated in 1.0 M  $\text{Na}_2\text{CO}_3$  from room temperature to 300°C (Figure 1). Subsequent changes which occurred as the treatment was continued at 300°C are also reflected in Figure 1. The data in this diagram represent the results of nine different runs conducted for various time intervals. The results show that by the time the reaction mixture had reached 300°C the sulfur content of the coal had been reduced by 56% which was equivalent to removing all of the inorganic sulfur. As the treatment was continued at 300°C, the sulfur content of the coal was further reduced until a reduction of 69% was achieved. Further treatment was counterproductive as the sulfur content of the product actually increased slightly. Thus for maximizing sulfur removal, the optimum treatment time was 85 min. total or 40 min. beyond the initial heat up period. For the optimum treatment time, the total sulfur content of the alkali-treated coal was 27% below the apparent organic sulfur content of 1.13% indicated in Table 1 for the raw coal. Hence, it appeared that some of the organic sulfur had been removed.

The ash content of the alkali-treated coal was slightly higher than that of the raw coal which was probably due to the formation of sodium hydroaluminosilicates. Coal recovery on a moisture- and ash-free basis declined gradually as the treatment time was extended (Figure 1). Moreover, the rate of decline increased beyond a total treatment time of 70 min.

When the alkali-treated coal which had provided the data for Figure 1 was subsequently leached for 30 min. with boiling  $\text{HNO}_3$ , the overall results shown in Figure 2 were obtained for the two-step process. The time and temperature of the alkaline

treatment step are indicated. Since the  $\text{HNO}_3$  leaching step by itself was capable of removing the inorganic sulfur and reducing the total sulfur content of the coal by 57%, treating the coal with alkali first had a relatively small effect on the total sulfur content of the coal after the combined treatment. For the optimum alkaline treatment time, the total sulfur content was reduced 77.5% by the combined treatment, as compared to 69% for the alkaline leaching step alone. On the other hand, the combined treatment seemed to account for a significant reduction in the apparent organic sulfur content. For an extended treatment time, the reduction in organic sulfur content exceeded 45% for the combined treatment which seemed significantly greater than the 27% reduction noted for the alkaline leaching step alone.

The alkaline treatment step had a pronounced effect on what happened to the ash content of Cherokee coal when it was subsequently leached with acid. As Figure 2 indicates,  $\text{HNO}_3$  leaching of the raw coal reduced the ash content 63%. Pretreating the coal with alkali for short intervals at temperatures up to  $200^\circ\text{C}$  had little effect on the results of subsequent acid leaching. But pretreating the coal at  $300^\circ\text{C}$  for even a short time resulted in lowering the ash content 90% when the coal was leached with acid.

To determine the effect of the final temperature during the alkaline leaching of Cherokee coal, several runs were carried out in which different portions of the coal were treated with  $1.0\text{ M Na}_2\text{CO}_3$  for 1.0 hr. at various final temperatures. The alkali-treated coal was then leached with  $\text{HNO}_3$ . The results of the alkaline leaching step are indicated in Figure 3 and the overall results in Figure 4. As the treatment temperature was raised, the quantity of sulfur removed by the first step increased greatly while coal recovery declined. The decline in recovery was gradual up to  $250^\circ\text{C}$  and then more precipitous beyond. The overall reduction in total sulfur content for both steps increased slightly and the reduction in apparent organic sulfur content somewhat more as the temperature of the first step was raised. The overall reduction in ash content for both steps also rose but then reached a plateau at  $250^\circ\text{C}$ .

The effects of alkali type and concentration were studied by treating different portions of Cherokee coal with various alkaline solutions for 1 hr. at  $300^\circ\text{C}$  (Table 2) and then by leaching with  $\text{HNO}_3$ . The sulfur reduction achieved in the first step was nearly the same for a majority of the alkalis; however, it was slightly lower for coal treated with either  $\text{NaHCO}_3$  or  $\text{KHCO}_3$ . Coal recovery in the first step was similar with most alkalis except that it was slightly higher for coal treated with  $\text{Na}_2\text{HCO}_3$  and greatly lower for coal treated with  $\text{NaOH}$ . Because of the low recovery, the caustic-treated coal was not subjected to the second step. When the second step was applied to the other alkali-treated portions, the lowest sulfur and ash contents were obtained with coal treated with  $1.0\text{ M Na}_2\text{CO}_3$ . Lower concentrations of  $\text{Na}_2\text{CO}_3$  achieved similar overall reductions in sulfur and ash contents and provided a higher recovery.

Other coals were also subjected to the two-step treatment (see Table 3). The results obtained with ball-milled Illinois No. 6 coal were similar, in general, to those achieved with Cherokee coal. When the alkaline treatment step was applied to either coal, sulfur reduction increased and coal recovery declined as the temperature was raised. However, for any given temperature the recovery and sulfur content of the alkali-treated product were higher for Illinois coal than for Cherokee coal. The high sulfur content of the treated Illinois coal appeared to be largely due to the higher organic sulfur content of the raw coal, while the higher recovery of this material seemed to be related to a difference in coal rank. When the alkali-treated Illinois coal was treated with  $\text{HNO}_3$ , most of the ash-forming minerals were removed to give a low ash content. Also, the total sulfur content of the final product was lower than the apparent organic sulfur content of the raw coal, indicating removal of some organic sulfur. As for Cherokee coal, the results with Illinois coal were

not affected greatly by alkali concentration, but in both cases the final ash content achieved with the two-step process declined slightly as the alkali concentration increased. The results with Illinois coal were also not affected greatly by particle size. The first-step recovery was slightly lower and the ash-content of the final product was slightly higher for -200 mesh coal than for -400 mesh coal. The sulfur content of the final product was nearly the same in both cases.

Compared to the other coals, Lower Kittanning coal responded similarly in some ways to the two-step treatment but differently in other ways (Table 3). The differences seemed related to the high ash and sulfur contents of the coal and possibly to a difference in mineral species. Sulfur removal was affected by the alkaline treatment time and temperature much as for the other coals. However, because of the very high iron pyrite content, the alkaline leaching step never succeeded in reducing the total sulfur content to the level of the apparent organic sulfur content. On the other hand, after applying both steps, the final sulfur content was always below the apparent organic sulfur content of the raw coal again indicating organic sulfur removal. Sulfur removal in the first step was affected somewhat by alkali concentration and a 1.0 M concentration appeared optimum. Coal recovery was affected by changes in various parameters as for the other coals, but it was slightly higher for any given set of conditions in the case of Lower Kittanning coal. The greatest difference in results with this coal occurred with the removal of ash-forming minerals, because the alkaline treatment step appeared ineffective except under relatively mild conditions. The removal of ash-forming minerals by acid leaching was not improved by the first step in most cases. Only by carrying out the first step at a relatively moderate temperature (i.e., 250°C) or with the smallest alkali concentration or for the shortest time did it appear to have a beneficial effect on the overall results. Consequently it seemed as though the Lower Kittanning coal was unique in containing some component which reacted with alkali under more rigorous conditions to form an acid insoluble material.

#### DISCUSSION AND CONCLUSIONS

A two-step process for extracting mineral matter and sulfur from coal was demonstrated with three different coals under a variety of treatment conditions. The first step involves treatment with a hot alkaline solution which extracts part of the sulfur and generally converts much of the mineral matter to an acid-soluble form. The second step involves leaching with an acid to extract the converted mineral matter. Although  $\text{H}_2\text{SO}_4$  would likely be used in the second step of a commercial process,  $\text{HNO}_3$  was chosen for the present study in order to shed some light on the disposition of organic sulfur.

A major concern of the present study was the effect of various parameters involved in the alkaline treatment step. Early in the investigation it was observed that  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{NaOH}$  were equally effective for removing sulfur in the first step while  $\text{NaHCO}_3$  and  $\text{KHCO}_3$  were less effective. On the other hand, coal recovery suffered greatly when  $\text{NaOH}$  was used. For the combined two-step treatment, the lowest sulfur and ash contents were achieved with  $\text{Na}_2\text{CO}_3$ . In view of this result and various economic advantages,  $\text{Na}_2\text{CO}_3$  was selected for studying the effects of other parameters. The effects of alkali concentration appeared relatively minor in most instances. However, for Lower Kittanning coal an alkali concentration of 1.0 M appeared optimum for removing sulfur in the first step whereas a smaller concentration (0.2 M) resulted in a lower ash content overall for the two-step process.

Alkali-treatment time and temperature affected the results greatly. Sulfur removal increased and coal recovery decreased in the first step with rising temperature, and above 250°C coal recovery decreased disproportionately. Removal of mineral matter in the second step was affected by the temperature of the first step. With both the Iowa and Illinois coals, the overall reduction in ash content for both steps increased with temperature up to 300°C and then leveled off. But with Lower

Kittanning coal 250°C seemed to be the optimum temperature for reducing the ash content. Increasing the alkaline treatment time up to a point resulted in increasing sulfur removal in the first step, but beyond this point less sulfur was removed. Coal recovery declined as the alkaline treatment time was extended, and the rate of decline accelerated after prolonged treatment.

The apparent removal of organic sulfur by the two-step treatment observed with all three coals was of considerable interest. Since the total sulfur content of the treated coal was below that which could be achieved by leaching with  $\text{HNO}_3$  alone, it appeared that the alkaline leaching step either removed a significant quantity of organic sulfur or converted some of the organic sulfur into a form which was extractable with  $\text{HNO}_3$ . In several instances the total sulfur content of Iowa or Illinois coal treated by the alkaline leaching step alone was below the apparent organic sulfur content of the raw coal indicating organic sulfur removal as well as inorganic sulfur removal, but usually the apparent reduction in organic sulfur content was slight and may not have been significant.

Lower Kittanning coal was unusual in that less rigorous alkaline treatment conditions were more effective than more rigorous conditions for converting the mineral matter into a form extractable with nitric acid. Additional work is needed to explain these unusual results.

#### ACKNOWLEDGEMENT

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Table 1. Bituminous coals used in leaching experiments

Coal Seam	Location	Size mesh	Ash, %	Tot. S %	HNO <sub>3</sub> leached	
					Ash, %	Tot. S %
Cherokee group	Monroe County, Iowa	-400	8.24	2.65	3.05	1.13
Illinois No. 6	Trivoli County, Illinois	-200	12.75	3.71	5.55	1.66
		-400	8.90	3.14	4.99	1.66
Lower Kittanning	Armstrong County, Pennsylvania	-200	18.07	10.44	7.94	1.88
		-400	18.44	10.24	8.29	1.69

Table 2. Results of treating Cherokee coal with different alkalis at 300°C for 1 hr. followed by leaching with HNO<sub>3</sub>

Alkali	Alkaline treatment step				Product <sup>a</sup>		Overall reduction		
	Recov., %	Ash, %	Tot. S %	S redn., %	Ash, %	Tot. S, %	Ash, %	Tot. S, %	Org. S, %
0.2 M Na <sub>2</sub> CO <sub>3</sub>	85.8	10.04	0.94	64.5	1.21	0.62	85.3	76.6	45.1
0.6 M Na <sub>2</sub> CO <sub>3</sub>	85.4	10.32	0.84	68.3	0.95	0.62	88.5	76.6	45.1
1.0 M Na <sub>2</sub> CO <sub>3</sub>	78.7	11.90	0.92	65.3	0.88	0.62	89.3	76.6	45.1
1.0 M NaHCO <sub>3</sub>	84.0	10.42	1.35	49.1	1.10	0.84	86.7	68.3	25.7
1.0 M K <sub>2</sub> CO <sub>3</sub>	79.4	11.84	1.02	61.5	1.63	0.83	80.2	68.7	26.5
1.0 M KHCO <sub>3</sub>	75.4	13.13	1.27	52.1	2.15	0.80	73.9	69.8	29.2
2.8 M NaOH	35.6	13.42	1.02	61.5	--	--	--	--	--

<sup>a</sup> Ash and total sulfur contents of final acid-treated product.

Table 3. Results of applying different alkaline treatment conditions to coal followed by leaching with  $\text{HNO}_3$ .

Coal	$\text{Na}_2\text{CO}_3$ M	Temp., °C	Time, min.	Alkaline treatment step <sup>a</sup>			Acid trtd. prod.			Overall reduction		
				Recovery, %	Ash, %	Tot. S, %	Ash, %	Tot. S, %	Ash, %	Tot. S, %	Org. S, %	Org. S, %
Ill. No. 6	0.2	300	60	89.8	11.73	2.03	35.4	1.44	1.43	83.8	54.5	13.9
Ill. No. 6	0.6	300	60	89.5	11.66	1.68	46.5	1.04	1.43	88.3	54.5	13.9
Ill. No. 6	1.0	250	60	96.8	11.34	1.91	39.2	1.03	1.30	88.4	58.6	21.7
Ill. No. 6	1.0	300	60	86.8	12.09	1.78	43.3	0.77	1.44	91.3	54.1	13.3
Ill. No. 6	1.0	344	60	80.8	11.36	1.36	56.7	0.71	1.02	92.0	67.5	38.6
Ill. No. 6 <sup>b</sup>	1.0	300	60	81.2	19.42	1.95	47.4	1.43	1.39	88.8	62.5	16.3
Low. Kit.	0.2	300	60	91.5	20.67	5.74	43.9	4.02	1.52	78.2	85.2	10.1
Low. Kit.	0.6	300	60	90.0	21.80	3.16	69.1	8.92	1.26	51.6	87.7	25.4
Low. Kit.	1.0	300	60	88.8	23.40	3.03	70.4	8.98	1.31	51.3	87.2	22.5
Low. Kit.	2.0	300	60	89.8	22.94	3.30	67.8	8.62	1.27	53.3	87.6	24.9
Low. Kit.	3.0	300	60	87.2	24.57	3.96	61.3	8.15	1.44	55.8	85.9	14.8
Low. Kit.	1.0	200	60	97.0	18.99	9.23	9.9	3.29	1.62	82.2	84.2	4.1
Low. Kit.	1.0	250	60	96.5	20.78	7.88	23.0	2.88	1.45	84.4	85.8	14.2
Low. Kit.	1.0	344	60	85.2	22.58	1.87	81.7	10.14	1.20	45.0	88.3	29.0
Low. Kit.	1.0	300	0	92.0	22.36	5.61	45.2	6.29	1.43	65.9	86.0	15.4
Low. Kit.	1.0	300	30	88.9	23.66	3.42	66.6	8.70	1.25	52.8	87.8	26.0
Low. Kit.	1.0	300	90	81.7	30.00	3.83	62.6	8.24	1.32	55.3	87.1	21.9
Low. Kit. <sup>b</sup>	1.0	300	60	87.8	23.85	4.21	59.7	7.96	1.36	56.8	87.0	27.7

<sup>a</sup> Net treatment time at constant temperature is indicated.

<sup>b</sup> -200 mesh.

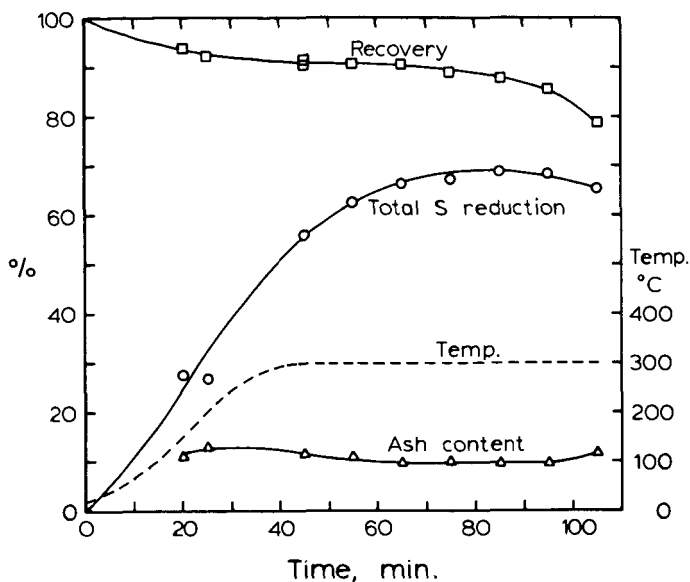


Figure 1. Results of treating -400 mesh Cherokee coal with 1 M  $\text{Na}_2\text{CO}_3$ .

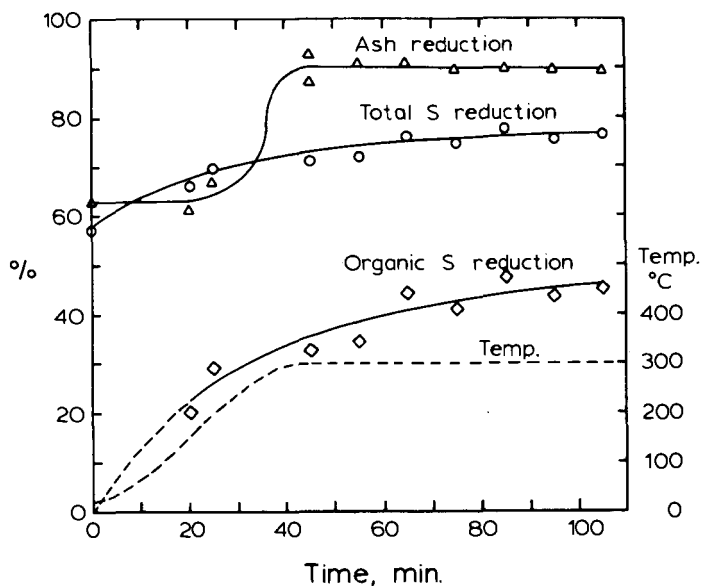


Figure 2. Overall results of applying the two-step process to Cherokee coal. Time and temperature are for the alkaline treatment step.



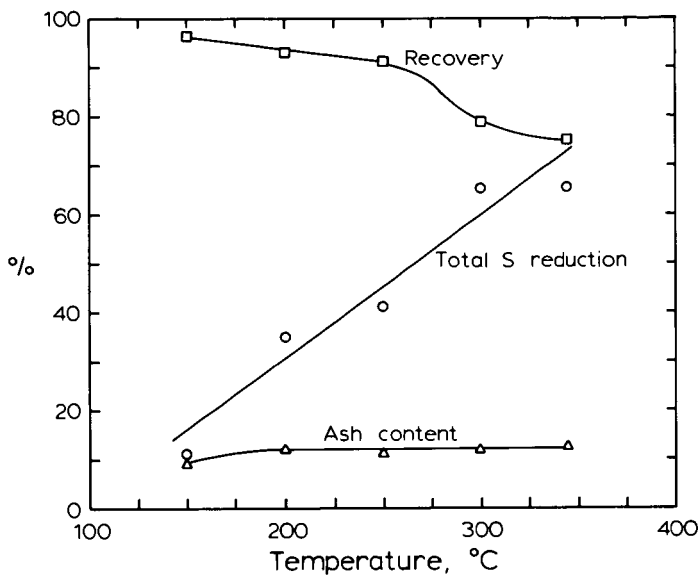


Figure 3. Results of treating -400 mesh Cherokee coal with 1 M Na<sub>2</sub>CO<sub>3</sub> for 1 hr. at indicated temperature.

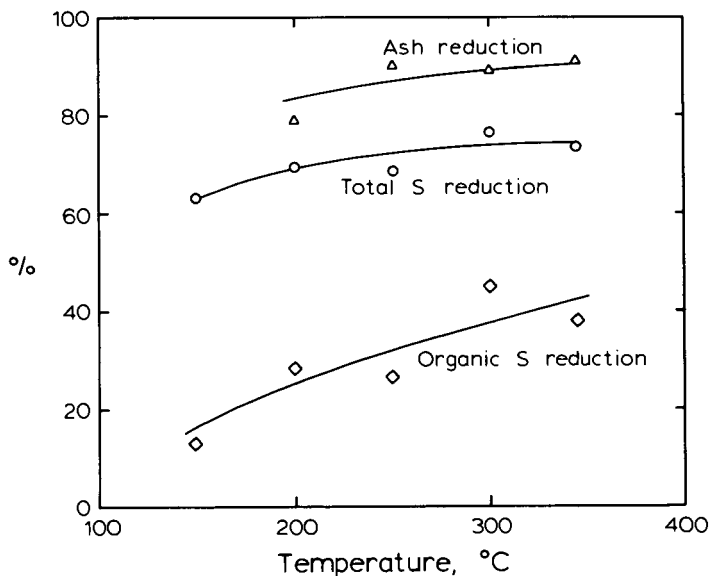


Figure 4. Overall results of applying the two-step process to Cherokee coal which was treated with Na<sub>2</sub>CO<sub>3</sub> at the indicated temperature.